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HIGH-TEMPERATURE HEATING ELEMENT AS WELL AS PROCESS FOR ITS PRODUCTION

[Hochtemperatur-Heizelement sowie Verfahren zu seiner Herstellung]

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High-temperature Heating Element as well as Process for its Production

The invention concerns a high-temperature heating element with a substrate of aluminum nitride and a heat conductor arranged thereon as well as a process for producing the heating element. High-temperature elements are used in the motor vehicle industry for producing ceramic heating devices, especially for producing glow plugs and glow attachments.

It is disadvantageous when using aluminum nitride ceramic for producing high-temperature heating elements that, due to the good heat conductivity of aluminum nitride through heat conduction, a highly increased heating capacity is required to maintain the heater at a predetermined temperature.

To reduce the heat conduction, the heating element of the invention has a substrate (1) of aluminum nitride, in which the substrate area (1a), which should be thermally insulating, is doted with foreign ions. The heat conductor (2) can consist of one of the usual heat conductors used in known high-temperature heating elements. As oxidation protection can serve a substrate

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[1] Numbers in the margin indicate pagination in the foreign text.

(4). A high-temperature heating element of the invention is show, for example, in Fig. 1.

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Description

The invention is based on a high-temperature heating element of the kind disclosed in the independent claim.

High-temperature elements of the kind disclosed in the independent claim are known to be used to a large extent in the motor vehicle industry to produce ceramic heating arrangements, in particular for glow plugs and glow attachments or incandescent bodies to, for example, facilitate as starter help the startup of diesel engines.

From DE-OS 35 12 483 is known, for example, a ceramic heating device consisting of a heating element made from a sintered body of a mixture of $MoSi_2$ powder and Si_3N_4 powder, a holding element of an electrically insulating ceramic sintered body, as well as an electric power supply arrangement. In the known heating arrangement, the heating element consists of a sintered body made from a mixture of $MoSi_2$ powder and Si_3N_4 powder, wherein the average particle diameter of the Si_3N_4 powder is greater than that of the $MoSi_2$ powder.

From DE-OS 30 11 297 are also known high-temperature heating elements made from a ceramic body of silicon nitride, sialon,

aluminum nitride, and silicon carbide with a metallic body in the form of a plate or a thread embedded therein, in which the metal is tungsten or molybdenum.

From DE-OS 33 35 144 is also known an inlet blowpipe for an internal combustion engine with a heating arrangement, which consists of a heat resistor of tungsten embedded in a ceramic material. The ceramic material can consist, for example, of silicon nitride (Si_3N_4).

From United States patent 4,035,613 are also known cylinder-shaped ceramic heating elements from a heat-resistant ceramic material such as aluminum oxide and fosterite as well as a resistance pattern produced thereon by the applied heat produced by a conductive metal, for example, molybdenum-manganese paste or tungsten paste.

From the Japanese patent publication 54-1 09 536 is also known a ceramic heater for glow plugs, which is comprised of circular plate-shaped ceramic plates and printed resistance bodies of molybdenum, tungsten, or manganese.

From DE-OS 33 07 109 is finally known a device for injecting fuel into combustion chambers, especially into the combustion chambers of diesel engines, with an injection nozzle and an incandescent body connected downstream wetted by a spray jet of fuel, in which the incandescent body is arranged on the side of

the face of the injection nozzle of the combustion chamber, and has a channel surrounded by heatable walls for the passage and partial evaporation of the fuel spray jet. The glow body can therefore be made of ceramic and the heating element is formed by a metallic coating layer applied on the ceramic surface.

It is further known, for example, from a work by N. Iwase and collaborators entitled: "Thick Film and Direct Bond Copper Forming Technologies for Aluminum Nitride Substrate," of Toshiba R & D Center 1, Toshiba-cho, Komukai Saiwaku, Kawasaki, Japan 210, to imprint in thick film technology on a substrates of A1N ceramic, which are characterized by a high heat conductivity, good electrical insulation up to high temperatures, great hardness, good mechanical properties, and good thermal shock resistance, and to use thick film plastics similar to those known for imprinting on substrates of Al_2O_3.

It is a disadvantage of the ceramic heating elements that they cannot be stressed up to very high temperatures, they do not have a sufficient thermal shock resistance, they do not adhere well to the heat conducting layers imprinted on the ceramic substrate and/or they are expensive to produce.

It is also disadvantageous when using aluminum nitride ceramic to produce high-temperature heating elements that, due to the good heat conductivity of aluminum nitride through heat

conduction from the heater area into the edge zones, in particular for a contacting (mount), require a highly increased heating capacity to maintain the heater at a predetermined temperature. The thermal stress on the contacts and the heater mount is also considerable.

Advantages of the Invention

The high-temperature heating element of the invention with the characterizing features of the independent claim has the advantage that the heat conduction from the heater area into the edge zones, in particular with regards to contacting, is clearly reduced. It has been shown, in this way, for example, that the heat conductivity can be clearly reduced by a suitable doting of about 150 W/mk up to about 10 W/mk.

The areas of the aluminum nitride substrate to be thermally insulated are doted in an advantageous manner with about 50 ppm to about 5% foreign ions. Especially advantageous doting ion concentrations are at about 50 ppm to 3%.

As doting ions are suitable in principle all the foreign ions that can be available in an A1N grid, for example, oxygen, boron, and silicon ions. Particularly suitable are those that make possible a good adaptation of the heat expansion coefficients to those of the A1N.

Silicon ions are used as doting ions according to an advantageous embodiment of the invention.

The aluminum nitride substrates that can be used for producing a high-temperature heating element according to the invention can contain as commercially available aluminum nitride substrates that contain, aside from aluminum nitride, also a bonding agent that degrades or evaporates at the sintering temperature, which also consist of so-called green pressed "aluminum nitride substrates" and sintered substrates and hot pressed rods.

The thickness and shape of the aluminum nitride substrates can be different. Films are used as substrates in an advantageous manner. The thickness of the films is 0.3 to 3 mm, in particular 0.5 to 2.0 mm.

The used aluminum nitride substrates can, if required, contain aside from bonding agents also other additives, for example, comparatively less quantities of sintering additives such as, for example, Y_2O_3.

The introduction of foreign ions into the areas of the aluminum nitride substrate, which should be thermally insulated, that is, the doting of these areas can take place in different ways.

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A first suitable method consists of an ion implantation. In this operating mode, ions, for example Si ions, are accelerated in an electromagnetic field and shot into the substrate at a high velocity through the AlN substrate surface.

A second particularly advantageous method consists in using a green pressed aluminum nitride substrate material for producing a high-temperature heating element and producing the substrate by adding a material, that is, a doting material, that delivers doting ions at the sintering temperature of the substrate material to part of the aluminum nitride substrate material to be compressed, compounding the substrate of doting and non-doting material, and compressing and sintering the compounded substrate material.

A particularly suitable doting material is silicon.

The doting material of the aluminum nitride to be doted is advantageously compounded at concentrations of 50 ppm to 5%.

The compression takes place preferably at pressures of 10 to 100 bar. The sintering takes place suitably at temperatures of 1600°C to 2000°C. The work is carried out preferably at temperatures of 1650°C to 1800°C. The sintering duration amounts suitably to 6, preferably 2 to 4 hours.

A third advantageous method of introducing foreign metal ions into the aluminum nitride substrate consists in that the doting

agent, for example in the form of a powder, precipitates on the desired areas of the surface of the aluminum nitride substrate, which is available, for example, in the form of a commercially available aluminum nitride film or a green pressed aluminum nitride substrate, and the doting ions are then diffused into the substrate material by heat treatment. The precipitation of the doting agent can take place, for example, by vapor deposition or such as, for example in the case of silicon, also by imprinting on thick film paste.

Suitable thick film pastes can be comprised of the doting material and an organic carrier, for example, 70 percent by weight doting material and 30 percent by weight organic carrier. The organic carrier corresponds therefore to the carriers which are used normally in thick film technology. The heat treatment by means of which the doting ions are diffused into the substrate material can persist, for example, for a 10-hour to 36-hour heating of the material to a temperature of about 1000 to 1400°C. It is heated in an advantageous manner for about 20 to 30 hours to a temperature of 1100 to 1300°C. The heat treatment takes place advantageously under a protective gas, for example argon, or in a vacuum.

The heat conductor together with the heater feed line can be made, for example, of MoMn or $MoSi_2$.

According to a particularly advantageous embodiment of the invention, the heat conductor together with the heater feed line consists of molybdenum disilicide into which are mixed, if required, substances for adjusting the electric resistance and/or to improve the adaptation of the thermal expansion coefficient in subordinate quantities such as, for example, aluminum oxide and aluminum nitride.

The production of a high-temperature heating element according to the invention can take place consequently in an advantageous manner by doting the areas of an aluminum nitride substrate, which should be thermally insulated, according to one of the disclosed methods with foreign ions, imprinting a heater feed line, preferably in thin film technology, on the doted areas or imprinting a heat conductor on the non-doted areas, and sintering the imprinted substrate under a protective gas, and seasoning the same thereafter. The sintering is carried out suitably at temperatures of 1500 to 1800°C, in particular 1600 to 1800°C.

The production of a high-temperature heating element according to the invention can take place in another advantageous embodiment, for example, however, also by imprinting a heat conductor with a heater feed line preferably in thin film technology on a substrate of aluminum nitride with

doted areas, as disclosed, by applying another substrate of aluminum nitride on the imprinted substrate of aluminum nitride, which is advantageously doted in the areas that come into contact with the heater feed line, and by sintering the substrates joined to a sandwich with the embedded heat conductor and the heater feed line.

According to another advantageous embodiment of the invention, it is proceeded in such a way that the areas to be thermally insulated are doted by adding a doting material to the paste used to configure the heater feed line and the doting ions are allowed to diffuse out of the applied paste during the sintering process into the aluminum substrate.

To the pastes used together with the heater feed line in thin film technology, for example molybdenum silicide pastes, for the production of the heat conductor can also be added substances for adjusting the electric resistance and/or to improve the adaptation of the thermal expansion coefficient.

A high-temperature heating element according to the invention with a molybdenum silicide heat conductor has the particular advantage that, because of the comparatively inexpensive heat conducting material, it is economical to produce, that it can be stressed at high temperatures (approx. 1400°C), that the molybdenum silicide adheres considerably better on the aluminum

nitride than on silicon nitride, that a uniform temperature distribution is achieved with very good conduction of the substrate, and that it has a high thermal shock resistance.

A high-temperature heating element of the invention can be used for producing ceramic heating devices of the most different types and for the most different application purposes. It is of particular importance for the motor vehicle industry where the heating element for the production of glow plugs, glow attachments, and incandescent bodies as well as inlet blowpipes can be used, to facilitate, for example, the startup of diesel engines. This means that a high-temperature heating element according to the invention is installed in a holder element of the usually known design and can be connected to a usually known power supply arrangement.

The production of a high-temperature heating element of the invention can be accomplished by machining in multiple printed panels. The width of a heating element is advantageously 3 to 10 mm and the length is 10 to 50 mm.

When used in a heater plug, the heating element of the invention is preferably designed as a rotation-symmetric body, wherein the printed conductor, for example, a molybdenum silicide printed conductor, was imprinted on a

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compact aluminum nitride pin, for example of hot pressed aluminum nitride, or on a film that was rolled up to a compact pin.

In the case of a heater plug, the diameter of the heating element amounts suitably to between 3 and 6 mm, the projection length amounts to between 10 and 30 mm, and the pin length amounts to between 20 and 60 mm.

Drawing

Three exemplary embodiments of the invention are shown in the drawings and are explained in more detail in the following description.

In the drawings, Fig. 1 shows a first exemplary embodiment of a heating element of the invention with a comparatively rigid A1N substrate film, Fig. 2 shows a second exemplary embodiment of a heating element of the invention with a flexible A1N substrate film in a correspondingly simplified illustration, and Fig. 3 shows a heater plug with a heating element in accordance with the invention.

Description of the Exemplary Embodiments

The high-temperature heating element of the invention shown simplified and highly enlarged in Fig. 1 consists of a substrate 1, for example, a commercially available A1N film with a thickness of, for example 1 mm, with a thermally insulating area

1a, on which have been imprinted by silk-screen printing, preferably screen printing or pad printing, the heat conductor 2 including the heater feed line together with the contact surfaces 3a and 3b. In the case shown, the heat conductor has a meandering shape. The heat conductor can, however, have any desired shape.

The thermally insulating area 1a shown with the dashed line was produced as follows:

The doting agent, for example silicon, was applied first on the surface by vapor deposition in the area 1a to be insulated or by means of a thin film paste on the aluminum nitride substrate in the area 1a to be insulated and was then allowed to diffuse by means of a heat treatment, for example, under an argon protective gas or in a vacuum at 1200°C over a period of several hours, for example, 24 hours.

To imprint the heat conductor with the heater feed line was used a molybdenum silicide paste with the following composition:

69.8 percent by weight commercially available $MoSi_2$ powder,

30.2 percent by weight thick oil consisting of:

6.0 percent by weight ethylcellulose,

79.0 percent by weight α-terpinol, and

15.0 percent by weight benzyl alcohol.

On the substrate treated in this way was then applied, after drying the heat conducting layer, a second non-imprinted substrate 4 of equal thickness in such a way that the contact surfaces 3a and 3b were not covered. The joined substrates were then sintered under a pressure of 5 mbar at a temperature of 1600°C in an atmosphere of N_2 with 10% H_2 for two hours. The substrate 4 served as oxidation protection.

A covering of the imprinted substrate 1 with the substrate 4 can be omitted especially if the substrate 1 is sintered with the imprinted heat conductor 2 under a protective gas, in particular a forming gas, at a temperature between 1600°C and 1800°C and then subjected to a seasoning process. The seasoning process can consist, for example, in annealing the imprinted and sintered substrate for 2 to 6 hours in an oxidizing atmosphere. Such a treatment leads to the formation of a SiO_2 protective layer, which protects for the most part the heat conductor being attacked in the oxidizing and reducing atmosphere.

It is unimportant if the imprinted substrate 1 is covered with a second substrate 4 or not, in which case the heat conductors adhere firmly to the A1N substrate on which they are applied.

The contact surfaces can be metallized in the usual manner. The contacting of the heat conductor takes place by means of the protective gas combustible thick film pastes on Cu, Ni, or Au base or by currentless deposition of Ni or Cu.

The heating element shown schematically in Fig. 2 differs from the heating element shown schematically in Fig. 1 essentially in that the A1N substrate consists of a green flexible A1N film 5. After doting the area 1a to be insulated and after imprinting the heat conductor 6 together with the heater feed line with the contact surfaces 7a and 7b on the thermally insulated area 1a, a layer that is approximately 20 μm thick of a paste of 10 to 50% A1N powder was imprinted on the part of the film 5 that carries the heat conductor 6 in an organic bonding agent, for example, ethylcellulose, α-terpinol, and benzyl alcohol.

The imprinted substrate shown schematically in Fig. 2 was then wound. The wound element was then sintered for 4 to 6 hours at a temperature within the range of 1650°C to 1800°C. The contacting surfaces 7a and 7b were then metallized.

The heater plug shown in Fig. 3 consists essentially of the plug housing 8, the heating element 9 of the aluminum nitride rod 10 with imprinted molybdenum silicide heat conductor 11,

which is imprinted on the sleeve 12 (⊕-connection) welded on the aluminum nitride rod 10, the insulation 14 of the heat conductor 11 against the ⊕-connection, the insulating disk 15, the round nut 16, and the terminal stud 17. The area 18 of the aluminum rod 10 shown hatched is the area doted with the foreign ions.

Patent Claims

1. A high-temperature heating element with a substrate of aluminum nitride and a heat conductor applied thereon, wherein the substrate areas, which are to be thermally insulated, are doted with foreign ions.
2. The high-temperature heating element of claim 1, wherein the substrate areas that are to be thermally insulated are doted with 50 ppm to 5% foreign ions.
3. The high-temperature heating element of one of the claims 1 to 2, wherein the substrate areas that are to be thermally insulated are doted with silicon ions as foreign ions.
4. A process for producing a high-temperature heating element according to claims 1 to 3, wherein a heat conductor is imprinted on a substrate of aluminum nitride in thick film technology, and the imprinted substrate is sintered under a protective gas, wherein the areas of the substrate that are to be thermally insulated are doted with foreign ions before the substrate is imprinted with the heat conductor.

5. The process of claim 4, wherein the substrate with the areas to be thermally insulated is produced by mixing the substances that produce foreign ions into the aluminum nitride that forms the areas of the substrate to be thermally insulated and by forming, compressing, and sintering the substrate from the aluminum nitride contained in the material that produces foreign ions and the aluminum nitride that contains material that does not produce foreign ions.

6. The process of claim 4, wherein the substrate with the areas to be thermally insulated is produced by applying doting agents in a thick film paste application on the areas to be insulated and that the foreign ions are allowed to diffuse into the substrate by heat treatment.

7. The process of claim 4, wherein the substrate with the areas that are to be thermally insulated is produced in that the doting agents are vapor-deposited on the areas to be insulated and the foreign ions are allowed to diffuse into the substrate by heat treatment.

8. The process of claim 7, wherein Si is vapor-deposited as doting agent on the areas to be insulated.

9. The process of claims 6 to 8, wherein the vapor-deposited material or the material provided with a thick film paste is heated for the purpose of a diffusion of the foreign ions under a protective gas or in a vacuum for 12 to 35 hours at a temperature of 800 to 1400°C.

10. The process for producing a high-temperature heating element according to claims 1 to 3, wherein a heat conductor is imprinted on a substrate of aluminum nitride in thick film technology and the imprinted substrate is sintered under a protective gas, wherein a substance is added to the printing paste used for imprinting the heater feed line, which delivers foreign ions that diffuse into the substrate during sintering.

11. The process of claim 10, wherein silicon is added to the printing paste.

12. The process of one of the claims 4 to 11, wherein films, plates, or cylindrical rods are used as aluminum nitride substrates.

2 sheets of drawing are attached

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DRAWINGS PAGE 1

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FIG.1

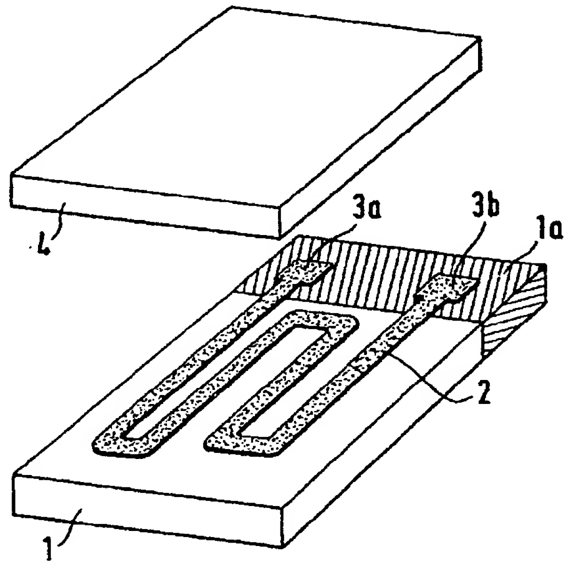

FIG.2

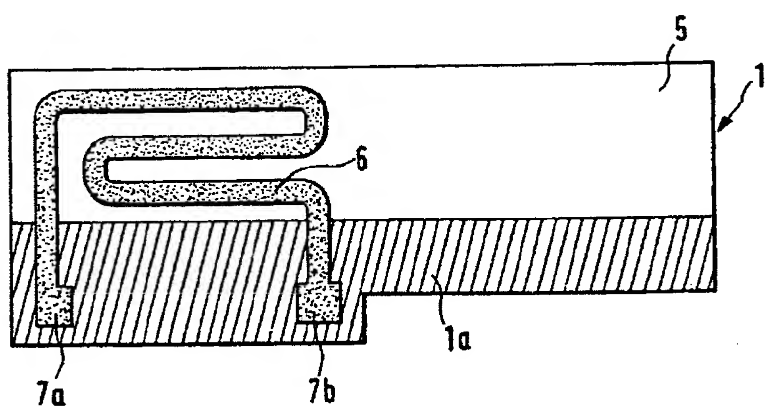

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FIG.3